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Customer No. 22,852
Attorney Docket No. 1435-120

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)
Manfred Bochmann et al.	) Group Art Unit: 1713
Serial No.: 09/924,603	) Examiner: Not Yet Assigned
Filed: August 9, 2001	)
For: Metal Complexes as Catalyst Component for Olefin Polymerization	)

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Commissioner for Patents and Trademarks
Washington, DC 20231

CLAIM FOR PRIORITY

Sir:

Under the provisions of Section 119 of 35 U.S.C., Applicants hereby claim the benefit of the filing date of United Kingdom Patent Application Number 9902697.3, filed February 9, 1999, for the above identified United States Patent Application.

In support of Applicants' claim for priority, a certified copy of the priority application is filed herewith.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: November 2, 2001

By: [signature]
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1. Your reference	9103
2. Patent application number *(The Patent Office will fill in this part)*	**9902697.3**
3. Full name, address and postcode of the or of each applicant *(underline all surnames)*	BP CHEMICALS LIMITED BRITANNIC HOUSE 1 FINSBURY CIRCUS LONDON EC2M 7BA
Patents ADP number *(if you know it)*	614189100 2.
If the applicant is a corporate body, give the country/state of its incorporation	ENGLAND, UNITED KINGDOM
4. Title of the invention	NOVEL COMPOUNDS
5. Name of your agent *(if you have one)*	SMITH, Julian Philip Howard
"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*	BP INTERNATIONAL LIMITED GROUP PATENTS & AGREEMENTS CHERTSEY ROAD SUNBURY-On-THAMES MIDDLESEX TW16 7LN
Patents ADP number *(if you know it)*	1855600 2

	Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*
6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number			

	Number of earlier application	Date of filing *(day / month / year)*
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8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:* *a) any applicant named in part 3 is not an inventor, or* *b) there is an inventor who is not named as an applicant, or* *c) any named applicant is a corporate body.* *See note (d))*	YES

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Claim(s)	-
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8

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11. I/We request the grant of a patent on the basis of this application.

Signature Date 8.2.99

SMITH, Julian Philip Howard

12. Name and daytime telephone number of person to contact in the United Kingdom

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NOVEL COMPOUNDS

The present invention relates to transition metal complex compounds, to polymerisation catalysts based thereon and to their use in the polymerisation and copolymerisation of olefins.

The use of certain transition metal compounds to polymerise 1-olefins, for example, ethylene, is well established in the prior art. The use of Ziegler-Natta catalysts, for example, those catalysts produced by activating titanium halides with organometallic compounds such as triethylaluminium, is fundamental to many commercial processes for manufacturing polyolefins. Over the last twenty or thirty years, advances in the technology have led to the development of Ziegler-Natta catalysts which have such high activities that olefin polymers and copolymers containing very low concentrations of residual catalyst can be produced directly in commercial polymerisation processes. The quantities of residual catalyst remaining in the produced polymer are so small as to render unnecessary their separation and removal for most commercial applications. Such processes can be operated by polymerising the monomers in the gas phase, or in solution or in suspension in a liquid hydrocarbon diluent. Polymerisation of the monomers can be carried out in the gas phase (the "gas phase process"), for example by fluidising under polymerisation conditions a bed comprising the target polyolefin powder and particles of the desired catalyst using a fluidising gas stream comprising the gaseous monomer. In the so-called "solution process" the (co)polymerisation is conducted by introducing the monomer into a solution or suspension of the catalyst in a liquid hydrocarbon diluent under conditions of temperature and pressure such that the produced polyolefin forms as a solution in the hydrocarbon diluent. In the "slurry process" the temperature, pressure and choice of diluent are such that the produced polymer forms as a suspension in the liquid hydrocarbon diluent. These

processes are generally operated at relatively low pressures (for example 10-50 bar) and low temperature (for example 50 to 150°C).

Commodity polyethylenes are commercially produced in a variety of different types and grades. Homopolymerisation of ethylene with transition metal based catalysts leads to the production of so-called "high density" grades of polyethylene. These polymers have relatively high stiffness and are useful for making articles where inherent rigidity is required. Copolymerisation of ethylene with higher 1-olefins (eg butene, hexene or octene) is employed commercially to provide a wide variety of copolymers differing in density and in other important physical properties. Particularly important copolymers made by copolymerising ethylene with higher 1-olefins using transition metal based catalysts are the copolymers having a density in the range of 0.91 to 0.93. These copolymers which are generally referred to in the art as "linear low density polyethylene" are in many respects similar to the so called "low density" polyethylene produced by the high pressure free radical catalysed polymerisation of ethylene. Such polymers and copolymers are used extensively in the manufacture of flexible blown film.

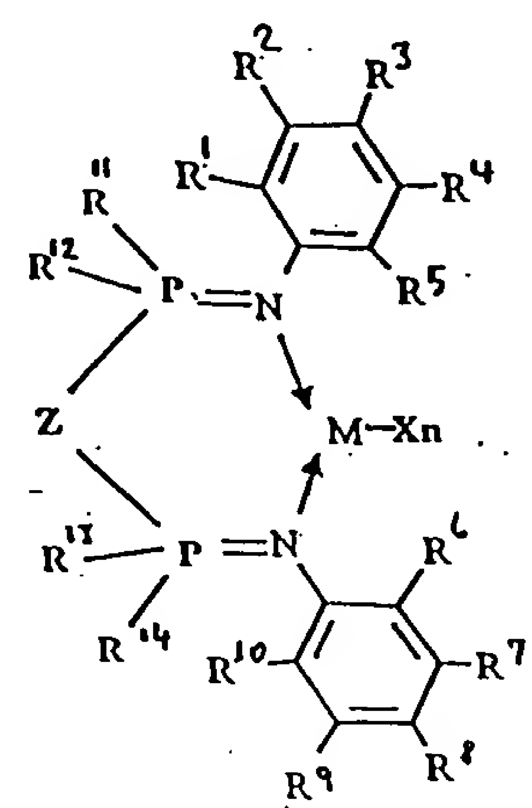
In recent years the use of certain metallocene catalysts (for example biscyclopentadienylzirconiumdichloride activated with alumoxane) has provided catalysts with potentially high activity. However, metallocene catalysts of this type suffer from a number of disadvantages, for example, high sensitivity to impurities when used with commercially available monomers, diluents and process gas streams, the need to use large quantities of expensive alumoxanes to achieve high activity, and difficulties in putting the catalyst on to a suitable support.

Patent Application WO98/27124 published on 25 June, 1998 discloses that ethylene may be polymerised by contacting it with certain iron or cobalt complexes of selected 2,6-pyridinecarboxaldehydebis(imines) and 2,6-diacylpyridinebis(imines).

An object of the present invention is to provide a novel catalyst suitable for polymerising monomers, for example, olefins, and especially for polymerising ethylene alone or for copolymerising ethylene with higher 1-olefins. A further object of the invention is to provide an improved process for the polymerisation of olefins, especially of ethylene alone or the copolymerisation of ethylene with higher 1-olefins to provide homopolymers and copolymers having controllable molecular weights. For example, using the catalysts of the present invention there can be made a wide variety of polyolefins such as, for example, liquid polyolefins,

oligomers linear alpha-olefins, resinous or tacky polyolefins, solid polyolefins suitable for making flexible film and solid polyolefins having high stiffness.

The present invention provide nitrogen containing transition metal complexes having the following Formula.



FORMULA I

wherein M is Fe[II], Fe[III], Ni[II], Co[I], Co[II], Co[III], V[III], Mn[I], Mn[II], Mn[III], Mn[IV], Ru[II], Ru[III] orRu[IV]; Pd[II], X represents an atom or group covalently or ionically bonded to the transition metal M; R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 and R^{10} are independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl; when any two or more of R^{11} R^{12}, R^{13}, or R^{14} are hydrocarbyl or aryl substituents.

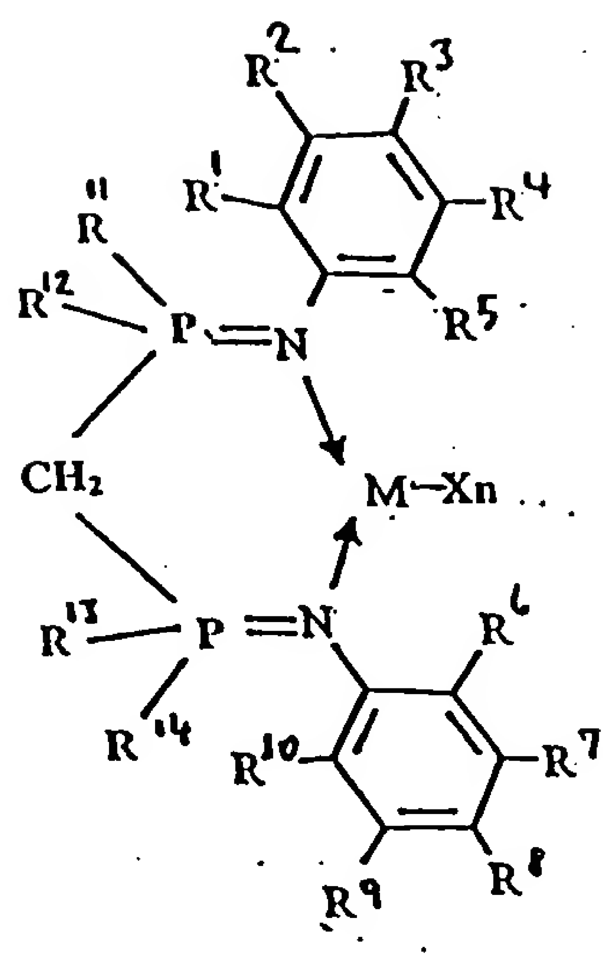
Z is a bridging group comprising a donor atom of N, P or S or alternatively is a neutral group comprising a C_1-C_4 alkylene group, a silyl or germyl group.

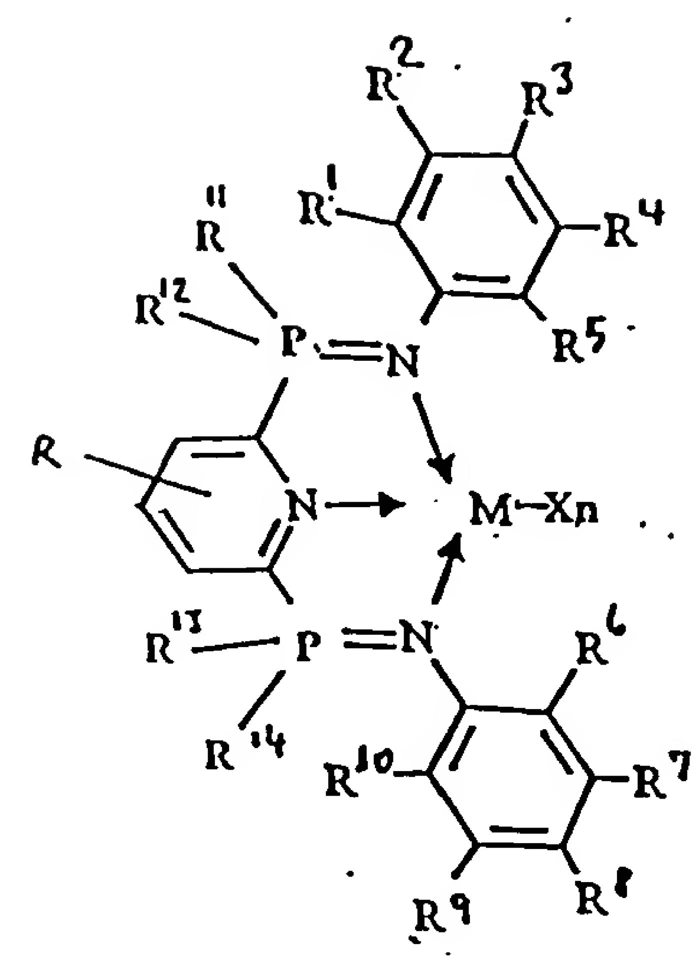
n = an integer to satisfy the valency of M.

Preferably at least one of R^1-R^{10} contains two or more carbon atoms and is preferably isopropyl.

The preferred bridging group Z is $-CH_2-$ or a donor atom of N preferably pyridyl.

In the preferred complexes the general formula may be represented by





The preferred metal atoms M are Fe, Ni or Co.

Preferred groups R^{11}-R^{14} are phenyl, alkyl, or cycloalkyl

Each of the nitrogen atoms is coordinated to the transition metal M by a "dative" bond, ie a bond formed by donation of a lone pair of electrons from the nitrogen atom. The remaining bonds on each nitrogen atom are covalent bonds formed by electron sharing between the nitrogen atoms and the organic ligand as shown in the defined formula for the transition metal complex illustrated above.

The atom or group represented by X in the compounds of the above Formulae can be, for example, selected from halide, sulphate, nitrate, thiolate, thiocarboxylate, BF_4^-, PF_6^-, hydride, hydrocarbyloxide, carboxylate, hydrocarbyl, substituted hydrocarbyl and heterohydrocarbyl. Examples of such atoms or groups are chloride, bromide, methyl , ethyl, propyl, butyl, octyl, decyl, phenyl, benzyl, methoxide, ethoxide, isopropoxide, tosylate, triflate, formate, acetate, phenoxide and benzoate. Preferred examples of the atom or group X in the compounds of Formula I are halide, for example, chloride, bromide; hydride; hydrocarbyloxide, for example, methoxide, ethoxide, isopropoxide, phenoxide; carboxylate, for example, formate, acetate, benzoate; hydrocarbyl, for example, methyl, ethyl, propyl, butyl, octyl, decyl, phenyl, benzyl; substituted hydrocarbyl; heterohydrocarbyl; tosylate; and triflate. Preferably X is selected from halide, hydride and hydrocarbyl or a chelating group eg. acetylacetonate. Chloride is particularly preferred.

The present invention further provides a polymerisation catalyst comprising

(1) a nitrogen-containing transition metal compound having the Formula I as hereinbefore defined, and

(2) an activating quantity of an activator compound.

The activator compound for the catalyst of the present invention is suitably selected from organoaluminium compounds and boron compounds. Suitable organoaluminium compounds include trialkyaluminium compounds, for example, trimethylaluminium, triethylaluminium, tributylaluminium, tri-n-octylaluminium, ethylaluminium dichloride, diethylaluminium chloride and alumoxanes. Alumoxanes are well known in the art as typically the oligomeric compounds which can be prepared by the controlled addition of water to an alkylaluminium compound, for example trimethylaluminium. Such compounds can be linear, cyclic or mixtures thereof. Commercially available alumoxanes are generally believed to be mixtures of linear and cyclic compounds. The cyclic alumoxanes can be represented by the formula $[R^{16}AlO]_s$ and the linear alumoxanes by the formula $R^{17}(R^{18}AlO)_s$ wherein s is a number from about 2 to 50, and wherein R^{16}, R^{17}, and R^{18} represent hydrocarbyl groups, preferably C_1 to C_6 alkyl groups, for example methyl, ethyl or butyl groups.

Examples of suitable boron compounds are dimethylphenylammoniumtetra(phenyl)borate, trityltetra(phenyl)borate, triphenylboron, dimethylphenylammonium tetra(pentafluorophenyl)borate, sodium tetrakis[(bis-3,5-trifluoromethyl)phenyl]borate, $H^+(OEt_2)$[(bis-3,5-trifluoromethyl)phenyl]borate, trityltetra(pentafluorophenyl)borate and tris(pentafluorophenyl) boron.

In the preparation of the catalysts of the present invention the quantity of activating compound selected from organoaluminium compounds and hydrocarbylboron compounds to be employed is easily determined by simple testing, for example, by the preparation of small test samples which can be used to polymerise small quantities of the monomer(s) and thus to determine the activity of the produced catalyst. It is generally found that the quantity employed is sufficient to provide 0.1 to 20,000 atoms, preferably 1 to 2000 atoms of aluminium or boron per Fe, Co, Mn or Ru metal atom in the compound of Formula Z.

A further aspect of the present invention provides a polymerisation catalyst system comprising (1) as the transition metal compound, a compound having the Formula I (2) an activating quantity of an activator compound selected from

organoaluminium and hydrocarbylboroncompounds and optionally (3) a neutral Lewis base.

In this further aspect of the present invention, the iron and cobalt compounds are preferred. The preferences in relation to the activator compound are the same as expressed above in relation to the catalyst of the present invention. Neutral Lewis bases are well known in the art of Ziegler-Natta catalyst polymerisation technology. Examples of classes of neutral Lewis bases suitably employed in the present invention are unsaturated hydrocarbons, for example, alkenes (other than 1-olefins) or alkynes, primary, secondary and tertiary amines, amides, phosphoramides, phosphines, phosphites, ethers, thioethers, nitriles, carbonyl compounds, for example, esters, ketones, aldehydes, carbon monoxide and carbon dioxide, sulphoxides, sulphones and boroxines. Although 1-olefins are capable of acting as neutral Lewis bases, for the purposes of the present invention they are regarded as monomer or comonomer 1-olefins and not as neutral Lewis bases *per se*. However, alkenes which are internal olefins, for example, 2-butene and cyclohexene are regarded as neutral Lewis bases in the present invention. Preferred Lewis bases are tertiary amines and aromatic esters, for example, dimethylaniline, diethylaniline, tributylamine, ethylbenzoate and benzylbenzoate. In this particular aspect of the present invention, components (1), (2) and (3) of the catalyst system can be brought together simultaneously or in any desired order. However, if components (2) and (3) are compounds which interact together strongly, for example, form a stable compound together, it is preferred to bring together either components (1) and (2) or components (1) and (3) in an initial step before introducing the final defined component. Preferably components (1) and (3) are contacted together before component (2) is introduced. The quantities of components (1) and (2) employed in the preparation of this catalyst system are suitably as described above in relation to the catalysts of the present invention. The quantity of the neutral Lewis Base [component (3)] is preferably such as to provide a ratio of component (1):component (3) in the range 100:1 to 1:1000, most preferably in the range 1:1 to 1:20. Components (1), (2) and (3) of the catalyst system can brought together, for example, as the neat materials, as a suspension or solution of the materials in a suitable diluent or solvent (for example a liquid hydrocarbon), or, if at least one of the components is volatile, by utilising the vapour of that component. The components can be brought together at any desired temperature. Mixing the components together at room temperature is

generally satisfactory. Heating to higher temperatures eg up to 120°C can be carried out if desired, eg to achieve better mixing of the components. It is preferred to carry out the bringing together of components (1), (2) and (3) in an inert atmosphere (eg dry nitrogen) or *in vacuo*. If it is desired to use the catalyst on a support material (see below), this can be achieved, for example, by preforming the catalyst system comprising components (1), (2) and (3) and impregnating the support material preferably with a solution thereof, or by introducing to the support material one or more of the components simultaneously or sequentially. If desired the support material itself can have the properties of a neutral Lewis base and can be employed as, or in place of, component (3). An example of a support material having neutral Lewis base properties is poly(aminostyrene) or a copolymer of styrene and aminostyrene (ie vinylaniline).

The catalysts of the present invention can if desired comprise more than one of the defined transition metal compounds.

In addition to said one or more defined transition metal compounds, the catalysts of the present invention can also include one or more other types of transition metal compounds or catalysts, for example, other nitrogen containing Fe or Co catalysts such as those described in our copending application PCT/GB98/02638. Examples of such other catalysts include 2,6-diacetylpyridinebis(2,4,6 trimethyl anil)$FeCl_2$.

The catalysts of the present invention can also include one or more other transition metal compounds, such as those of the type used in conventional Ziegler-Natta catalyst systems, metallocene-based catalysts, monocyclopentadienyl- or constrained geometry based catalysts, or heat activated supported chromium oxide catalysts (eg Phillips-type catalyst).

The catalysts of the present invention can be unsupported or supported on a support material, for example, silica, alumina, or zirconia, or on a polymer or prepolymer, for example polyethylene, polystyrene, or poly(aminostyrene).

If desired the catalysts can be formed in situ in the presence of the support material, or the support material can be pre-impregnated or premixed, simultaneously or sequentially, with one or more of the catalyst components. The catalysts of the present invention can if desired be supported on a heterogeneous catalyst, for example, a magnesium halide supported Ziegler Natta catalyst, a Phillips type (chromium oxide) supported catalyst or a supported metallocene catalyst. Formation of the supported catalyst can be achieved for example by

treating the transition metal compounds of the present invention with alumoxane in a suitable inert diluent, for example a volatile hydrocarbon, slurrying a particulate support material with the product and evaporating the volatile diluent. The produced supported catalyst is preferably in the form of a free-flowing powder. The quantity of support material employed can vary widely, for example from 100,000 to 1 grams per gram of metal present in the transition metal compound.

The present invention further provides a process for the polymerisation and copolymerisation of 1-olefins comprising contacting the monomeric olefin under polymerisation conditions with the polymerisation catalyst of the present invention.

The polymerisation conditions can be, for example, solution phase, slurry phase or gas phase. If desired, the catalyst can be used to polymerise ethylene under high pressure/high temperature process conditions wherein the polymeric material forms as a melt in supercritical ethylene. Preferably the polymerisation is conducted under gas phase fluidised bed conditions.

The polymerisation process may also involve a prepolymerisation procedure well known in the art.

Slurry phase polymerisation conditions or gas phase polymerisation conditions are particularly useful for the production of high density grades of polyethylene. In these processes the polymerisation conditions can be batch, continuous or semi-continuous. In the slurry phase process and the gas phase process, the catalyst is generally fed to the polymerisation zone in the form of a particulate solid. This solid can be, for example, an undiluted solid catalyst system formed from a nitrogen-containing complex and an activator, or can be the solid complex alone. In the latter situation, the activator can be fed to the polymerisation zone, for example as a solution, separately from or together with the solid complex. Preferably the catalyst system or the transition metal complex component of the catalyst system employed in the slurry polymerisation and gas phase polymerisation is supported on a support material. Most preferably the catalyst system is supported on a support material prior to its introduction into the polymerisation zone. Suitable support materials are, for example, silica, alumina, zirconia, talc, kieselguhr, or magnesia. Impregnation of the support material can be carried out by conventional techniques, for example, by forming a solution or suspension of the catalyst components in a suitable diluent or solvent, and slurrying the support material therewith. The support material thus impregnated with catalyst can then be separated from the diluent for example, by filtration or

evaporation techniques.

In the slurry phase polymerisation process the solid particles of catalyst, or supported catalyst, are fed to a polymerisation zone either as dry powder or as a slurry in the polymerisation diluent. Preferably the particles are fed to a polymerisation zone as a suspension in the polymerisation diluent. The polymerisation zone can be, for example, an autoclave or similar reaction vessel, or a continuous loop reactor, eg of the type well-know in the manufacture of polyethylene by the Phillips Process. When the polymerisation process of the present invention is carried out under slurry conditions the polymerisation is preferably carried out at a temperature above 0°C, most preferably above 15°C. The polymerisation temperature is preferably maintained below the temperature at which the polymer commences to soften or sinter in the presence of the polymerisation diluent. If the temperature is allowed to go above the latter temperature, fouling of the reactor can occur. Adjustment of the polymerisation within these defined temperature ranges can provide a useful means of controlling the average molecular weight of the produced polymer. A further useful means of controlling the molecular weight is to conduct the polymerisation in the presence of hydrogen gas which acts as chain transfer agent. Generally, the higher the concentration of hydrogen employed, the lower the average molecular weight of the produced polymer.

The use of hydrogen gas as a means of controlling the average molecular weight of the polymer or copolymer applies generally to the polymerisation process of the present invention. For example, hydrogen can be used to reduce the average molecular weight of polymers or copolymers prepared using gas phase, slurry phase or solution phase polymerisation conditions. The quantity of hydrogen gas to be employed to give the desired average molecular weight can be determined by simple "trial and error" polymerisation tests.

The polymerisation process of the present invention provides polymers and copolymers, especially ethylene polymers, at remarkably high productivity (based on the amount of polymer or copolymer produced per unit weight of nitrogen-containing transition metal complex employed in the catalyst system). This means that relatively very small quantities of transition metal complex are consumed in commercial processes using the process of the present invention. It also means that when the polymerisation process of the present invention is operated under polymer recovery conditions that do not employ a catalyst separation step, thus

leaving the catalyst, or residues thereof, in the polymer (eg as occurs in most commercial slurry and gas phase polymerisation processes), the amount of transition metal complex in the produced polymer can be very small. Experiments carried out with the catalyst of the present invention show that, for example, polymerisation of ethylene under slurry polymerisation conditions can provide a particulate polyethylene product containing catalyst so diluted by the produced polyethylene that the concentration of transition metal therein falls to, for example, 1 ppm or less wherein "ppm" is defined as parts by weight of transition metal per million parts by weight of polymer. Thus polyethylene produced within a polymerisation reactor by the process of the present invention may contain catalyst diluted with the polyethylene to such an extent that the transition metal content thereof is, for example, in the range of 10 - 0.001 ppm, preferably 5 - 0.01 ppm. Using a catalyst comprising a nitrogen-containing Fe complex in accordance with the present invention in, for example, a slurry polymerisation, it is possible to obtain polyethylene powder wherein the Fe concentration is, for example, 10 - 0.001 ppm, preferably 5 - 0.01 ppm.

Suitable monomers for use in the polymerisation process of the present invention are, for example, ethylene, propylene, butene, hexene, methyl methacrylate, methyl acrylate, butyl acrylate, acrylonitrile, vinyl acetate, and styrene. Preferred monomers for homopolymerisation processes are ethylene and propylene. The catalyst can also be used for copolymerising ethylene with other 1-olefins such as propylene, 1-butene, 1-hexene, 4-methylpentene-1, and octene.

The catalyst of the present invention can also be used for copolymerising ethylene with other monomeric materials, for example , methyl methacrylate, methyl acrylate, butyl acrylate, acrylonitrile, vinyl acetate, and styrene.

Methods for operating gas phase polymerisation processes are well known in the art. Such methods generally involve agitating (eg by stirring, vibrating or fluidising) a bed of catalyst, or a bed of the target polymer (ie polymer having the same or similar physical properties to that which it is desired to make in the polymerisation process) containing a catalyst, and feeding thereto a stream of monomer at least partially in the gaseous phase, under conditions such that at least part of the monomer polymerises in contact with the catalyst in the bed. The bed is generally cooled by the addition of cool gas (eg recycled gaseous monomer) and/or volatile liquid (eg a volatile inert hydrocarbon, or gaseous monomer which has been condensed to form a liquid). The polymer produced in, and isolated from,

gas phase processes forms directly a solid in the polymerisation zone and is free from, or substantially free from liquid. As is well known to those skilled in the art, if any liquid is allowed to enter the polymerisation zone of a gas phase polymerisation process the quantity of liquid is small in relation to the quantity of polymer present in the polymerisation zone. This is in contrast to "solution phase" processes wherein the polymer is formed dissolved in a solvent, and "slurry phase" processes wherein the polymer forms as a suspension in a liquid diluent.

The gas phase process can be operated under batch, semi-batch, or so-called "continuous" conditions. It is preferred to operate under conditions such that monomer is continuously recycled to an agitated polymerisation zone containing polymerisation catalyst, make-up monomer being provided to replace polymerised monomer, and continuously or intermittently withdrawing produced polymer from the polymerisation zone at a rate comparable to the rate of formation of the polymer, fresh catalyst being added to the polymerisation zone to replace the catalyst withdrawn from the polymerisation zone with the produced polymer.

Methods for operating gas phase fluidised bed processes for making polyethylene and ethylene copolymers are well known in the art. The process can be operated, for example, in a vertical cylindrical reactor equipped with a perforated distribution plate to support the bed and to distribute the incoming fluidising gas stream through the bed. The fluidising gas circulating through the bed serves to remove the heat of polymerisation from the bed and to supply monomer for polymerisation in the bed. Thus the fluidising gas generally comprises the monomer(s) normally together with some inert gas (eg nitrogen) and optionally with hydrogen as molecular weight modifier. The hot fluidising gas emerging from the top of the bed is led optionally through a velocity reduction zone (this can be a cylindrical portion of the reactor having a wider diameter) and, if desired, a cyclone and or filters to disentrain fine solid particles from the gas stream. The hot gas is then led to a heat exchanger to remove at least part of the heat of polymerisation. Catalyst is preferably fed continuously or at regular intervals to the bed. At start up of the process, the bed comprises fluidisable polymer which is preferably similar to the target polymer. Polymer is produced continuously within the bed by the polymerisation of the monomer(s). Preferably means are provided to discharge polymer from the bed continuously or at regular intervals to maintain the fluidised bed at the desired height. The process is generally operated at relatively low pressure, for example, at 10 to 50 bars, and at

temperatures for example, between 50 and 120 °C. The temperature of the bed is maintained below the sintering temperature of the fluidised polymer to avoid problems of agglomeration.

In the gas phase fluidised bed process for polymerisation of olefins the heat evolved by the exothermic polymerisation reaction is normally removed from the polymerisation zone (ie, the fluidised bed) by means of the fluidising gas stream as described above. The hot reactor gas emerging from the top of the bed is led through one or more heat exchangers wherein the gas is cooled. The cooled reactor gas, together with any make-up gas, is then recycled to the base of the bed. In the gas phase fluidised bed polymerisation process of the present invention it is desirable to provide additional cooling of the bed (and thereby improve the space time yield of the process) by feeding a volatile liquid to the bed under conditions such that the liquid evaporates in the bed thereby absorbing additional heat of polymerisation from the bed by the "latent heat of evaporation" effect. When the hot recycle gas from the bed enters the heat exchanger, the volatile liquid can condense out. In one embodiment of the present invention the volatile liquid is separated from the recycle gas and reintroduced separately into the bed. Thus, for example, the volatile liquid can be separated and sprayed into the bed. In another embodiment of the present invention the volatile liquid is recycled to the bed with the recycle gas. Thus the volatile liquid can be condensed from the fluidising gas stream emerging from the reactor and can be recycled to the bed with recycle gas, or can be separated from the recycle gas and sprayed back into the bed.

The method of condensing liquid in the recycle gas stream and returning the mixture of gas and entrained liquid to the bed is described in EP-A-0089691 and EP-A-0241947. It is preferred to reintroduce the condensed liquid into the bed separate from the recycle gas using the process described in our US Patent 5541270, the teaching of which is hereby incorporated into this specification,.

When using the catalysts of the present invention under gas phase polymerisation conditions, the catalyst, or one or more of the components employed to form the catalyst can, for example, be introduced into the polymerisation reaction zone in liquid form, for example, as a solution in an inert liquid diluent. Thus, for example, the transition metal component, or the activator component, or both of these components can be dissolved or slurried in a liquid diluent and fed to the polymerisation zone. Under these circumstances it is preferred the liquid containing the component(s) is sprayed as fine droplets into the

polymerisation zone. The droplet diameter is preferably within the range 1 to 1000 microns. EP-A-0593083, the teaching of which is hereby incorporated into this specification, discloses a process for introducing a polymerisation catalyst into a gas phase polymerisation. The methods disclosed in EP-A-0593083 can be suitably employed in the polymerisation process of the present invention if desired.

The present invention is illustrated in the following Examples and Comparative Examples. The reaction scheme for the preparation of the complexes of the present invention is shown in Figure 1.

<u>Experimental Section</u>

General Considerations. All manipulations were performed under a nitrogen atmosphere. Solvents were distilled under N_2 over sodium benzophenone (THF), sodium (toluene), Na/K alloy[diethyl ether, light petroleum (bp 40-60° C)], or CaH_2 (dichloromethane). NMR solvents were dried over activated molecular sieves and degassed through several freeze-thaw cycles. NMR spectra were recorded on Bruker ARX250 spectrometer. Chemical shifts are reported in ppm and referenced to residual solvent resonances (^1H, ^{13}C). Chemical shifts are relative to external 85% H_3PO_4 for ^{31}P data. The anilines, triphenylphosphine and 2,6-difluoropyridine were purchased from Aldrich. $NiBr_2 \cdot DME$ was prepared according to literature procedure. (Inorganic Synthesis 13, 162). Anhydrous $CoCl_2$ was purchased from Aldrich, but to ensure total dryness was heated under vacuum before use.

<u>Example 1</u>

<u>Synthesis of aniline azides, RN_3(Chem. Ber. 1958, 91, 2330)</u>

To a mixture of the 2,4,6-Me_3 C_6H_2 NH_2 (0.1 mol, 13.52 g) in 2M HCl and crushed ice was added sodium nitrite (0.107 mol, 7.38 g) dissolved in water. The solution was stirred for 20 min. Calcium carbonate was added to the diazonium salt, until the solution was neutralised. Sodium azide (0.116 mol, 7.54 g) in water was then added slowly and the solution stirred until no further effervescence was observed. The solution was extracted with 3 x 100 ml ether and the extracts combined and washed with sodium hydrogen carbonate solution before being dried over sodium sulphate. The solvent was removed under vacuum resulting in a red oil. The product was distilled as a yellow oil at 74-6°C/1mmHg

R = 2,4,6-Me_3-C_6H_2 (Yield: 11.32g, 0.07mol, 70%) ^1H NMR (250 MHz, $CDCl_3$ 20°C): δ 6.9(s, 2H), 2.4(s, 6H), 2.2(s, 3H). ^{13}C NMR (250 MHz, $CDCl_3$ 20°C): δ 135(C-N), 134(m-C_6H_5), 131(o-C_6H_5), 129(p-C_6H_5), 20(2Me), 17(Me)

Where R = 2,6-$^iPr_2(C_6H_3)$ the product was synthesized by the above procedure using 0.1 mol, 2,6-^iPr_z C_6 H_3 NH_2 17.73 g. The product a red oil is not distilled due to danger of explosion and is used in 3-3½ excess in the following procedures. ^{1}H NMR (250 MHz, $CDCl_3$ 20°C): δ 7.3(t, 2H), 7.2(d, 1H), 3.4(m, 2H), 1.3(d, 12H)

Example 2

Synthesis of 2,6-bis(diphenylphosphino)pyridine)

$PPh_2C_5H_3NPPh_2$ (Polyhedron 1990, 9, 1757)

To 1.0 mol sodium, approx. 1 l ammonia was condensed at -78°C . Triphenylphosphine (0.5 mol, 131 g) in 200 ml THF was added at -78°C dropwise over one hour. Ammonium chloride (0.5 mol, 26.8 g) was added in small portions and the mixture allowed to stir for a further hour at low temperature. 2,6-difluoropyridine in 100 ml THF was added dropwise and the solution stirred for a further hour. Toluene (200 ml) was then added and the mixture allowed to warm to room temperature and stirred overnight. The solution which was dark red in colour was then refluxed until no further ammonia could be detected (*ca.* 1 hour). The solvent was removed under vacuum leaving a red oil to which 200 ml methanol was added resulting in a creamy precipitate. This was filtered under air through a glass sinter and then dried under vacuum. The product was isolated as a cream powder (103.8 g, 0.23 mol, 93%). ^{1}H NMR (250 MHz, $CDCl_3$ 20°C): δ 7.25-7.36(m), 7.08(t), 7.05(t). ^{31}P NMR: (250MHz, $CDCl_3$): δ -5.0. Anal. Calcd for $C_{29}H_{23}NP_2$: C, 77.8; H, 5.14; N, 3.1; P, 13.8%. Found: C, 77.35; H, 5.01; N, 3.0; P, 13.7%. MS (EI): *m/z* 447 (M^+)

Example 3

Synthesis of 2,6-Bis(aryliminophosphino)pyridines

$ArNP(Ph)_2C_5H_3NP(Ph)_2NAr$ ($Ar=2,4,6\text{-}Me_3C_6H_2$)

To $PPh_2C_5H_3NPPh_2$, (0.014 mol, 6.26 g) in toluene at 60°C 2½ equivalents of 2,4,6-Me_3-$C_6H_2N_3$ (0.035 mol, 5.64 g) are added dropwise slowly and the solution stirred for 4 h at this temperature. The solvent was then removed under vacuum resulting in a brown oil, which was washed three times with ca. 100 ml of petrol leaving a cream solid which was dried under vacuum.

2,6-$C_5H_3N(PPh_2NR)_2$, R = 2,4,6 Me_3-C_6H_2

$C_{47}H_{45}N_3P_2$, (Yield: 7.8 g, 0.01 mols, 78%) ^{1}H NMR (250 MHz, $CDCl_3$ 20°C): δ 8.39(m), 7.89(m), 7.29-7.42(m), 7.11-7.42(m), 6.98(s, br), 2.14(s, 6H), 1.90 (s,12H). ^{31}P NMR: (250MHz, $CDCl_3$): δ -13.8. Anal. Calcd for $C_{47}H_{45}N_3P_2$:

C, 79.1; H, 6.3; N, 5.9; P, 8.7%. Found: C, 79.95; H, 6.26; N, 5.8; P, 8.6%. MS (EI): *m/z* 713 (M^+)

Example 4

For R = 2,6 $^iPr_2$-C_6H_3, the product was synthesized by the above procedure using $PPh_2C_5H_3NPPh_2$ (8.1 mmol, 3.65 g) and 3½ equivalents of $^iPr_2$-$C_5H_3N_3$ (28.35 mmol, 5.78 g).

2,6 $C_6H_3N(PPh_2NR)_2$ R=2,6 $^iPr_2$-C_6H_3

$C_{53}H_{57}N_3P_2$, (Yield: 3.4 g, 4 mmol, 54%) ^1H NMR (250 MHz, $CDCl_3$ 20°C): δ 8.40(m), 7.97(m), 7.30-7.44(m), 7.15-7.25(m), 6.96(d), 6.84(d), 6.81(t), 3.24(m, 4H), 0.86(d, 24H). ^{31}P NMR: (250MHz, $CDCl_3$): δ -13. Anal. Calcd for $C_{47}H_{45}N_3P_2$: C, 79.6; H, 7.1; N, 5.2; P, 7.7%. Found: C, 77.35; H, 7.05; N, 4.9; P, 7.45%. MS (EI): *m/z* 797 (M^+).

Example 5

Synthesis of MLX_2

Ni{2,6 $C_5H_3N(PPh_2NR)_2$}Br_2, R=2,6 $^iPr_2$-C_6H_3

To $NiBr_2$·DME (0.8m mol, 0.248 g) in THF, a slight excess of L (prepared in Example 4) (0.85m mol, 0.68 g) in THF was added at room temperature and immediate colour change was noticed and the solution stirred overnight. The solvent was removed under vacuum the resulting solids were washed with petrol and then crystallized from CH_2Cl_2. The product was isolated as an olive green powder. (Yield: 89%, 0.73 g, 0.71m mol). MS (FAB) *m/z* 936 (MLX^+).

Example 6

Ni{2,6-$C_5H_3N(PPh_2NR)_2$}Br_2, R = 2,4,6 Me_3-C_6H_2

This was synthesized by the above procedure using $NiBr_2$·DME (0.7 mol, 0.5 g) and L (0.75m mol, 0.53 g). The product was obtained as an olive green powder. (Yield: 70 %, 0.49m mol, 0.46 g). MS (FAB) *m/z* 936 (MLX^+).

Example 7

Co{2,6 $C_5H_3N(PPh_2NR)_2$}Cl_2 R=2,6 $^iPr_2$-C_6H_3

This was synthesized by the above procedure using $CoCl_2$ (0.7m mol, 0.091 g) and L (0.75m mol, 0.63 g). The product was obtained as an olive green powder. (Yield: 74 %, 0.56m mol, 0.52 g). MS (FAB) *m/z* 892 (MLX^+).

Example 8

Co{2,6-$C_5H_3N(PPh_2NR)_2$}Cl_2, R = 2,4,6 Me_3-C_6H_2

This was synthesized by the above procedure using $CoCl_2$ (0.7m mol, 0.09g) and L (0.75m mol, 0.53g). The product was obtained as a green powder. (Yield: 75 %, 0.53 mol, 0.44 g) MS (FAB) *m/z* 807 (MLX^+).

Example 9

$Fe\{2,6\ C_5H_3N(PPh_2NR)_2\}Br_2$, R= 2,4,6 Me_3-C_6H_2

To a mixture of $FeBr_2$ (0.8m mol, 0.212 g) and L (0.98m mol, 0.7 g) was added 40 ml of THF at room temperature. The colour slowly changed from orange to orange-red and the solution was stirred overnight. After filtration, the solvent of the filtrate was removed under vacuum and the resulting residue washed with toluene. The product was dried to give an olive green powder. (Yield: 56 %, 0.51 g,). FDMS *m/z* 929 (MLX_2^+), 850 (MLX^+).

Example 10

$Fe\{2,6\ C_5H_3N(PPh_2NR)_2\}Br_2$, R=2,6 $^iPr_2$-C_6H_3

The complex was prepared in analogy to above.

Synthesis of disphosphine di-imines (Phosphorus, Sulfur and Silicon, 1990, 47, 401).

Example 11

$C_{37}H_{32}N_2P_2$:

To dppm (diphenylphopshinomethane), (0.05mol, 19.59g) in toluene at 60°C 2 ½ equivalents of PhN_3(0.125 mol, 14.9 g) was added dropwise slowly and the solution stirred for 4 h at this temperature. The solvent was then removed in vacuo resulting in an oil, which was washed with petrol three times leaving a cream solid. The solid was dried under vacuum. (Yield: 25.4 g, 0.045 mol, 90 %). ^1H NMR (250 MHz,$CDCl_3$ 20°C): 8 (ppm): 7.70-7.75(m, 6H), 7.33-7.45(m, 12H), 7.00-7.06(m, 4H), 6.60-6.71(m, 8H), 3.74(t, ^2J(P.H) = 13.6 Hz). $^{31}P\{^1H\}$ NMR: (250MHz, $CDCl_3$): δ0.0. Anal. Calcd for $C_{29}H_{22}NP_2$: C, 78.4; H, 5.65; N, 4.95; P, 11.0%. Found: C, 77.7: H, 5.8; N, 4.85; P, 10.8%. MS(El): m/z 565 (M).

Example 12

$C_{43}H_{44}N_2P_2$:

This was synthesized by the above procedure using dppm (0.035 mol, 13.49 g) and 2 equivalents of 2,4,6 $Me_3.C_6H_2N_3$ (0.07 mol, 11.32 g). (Yield: 17.9g,0.027mol. 78%). ^1H NMR (250 MHz, $CDCl_3$ 20°C): 8 (ppm): 7.58-7.66(m, 8H), 7.30-7.33(m, 4H), 7.16-7.23(m, 8H), 6.71(s, 4H), 3.9(t, ^2J(P-H) = 14.4 Hz), 2.23(s, 6H), 1.95(s 12H) $^{31}P\{^1H\}$ NMR: (250MHz, $CDCl_3$): δ-15 ppm Anal. Calcd for $C_{43}H_{44}N_2P_2$: C,79.3;H, 6.7; N, 4.2; P, 9.7%. Found: C, 79.3; H, 6.8; N, 4.3; P,

9.5%. MS (E1): m/z 650 (M^+).

Example 13

$C_{49}H_{56}N_2P_2$:

This was synthesized by the above procedure using dppm (7.8mmol, 3.0 g) and 3 equivalents of 2,6 $^iPr_2$-$C_6H_3N_3$ (0.023mol, 4.67 g). (Yield: 4.6g, 6.2mmol, 80%). ^1H NMR (250 MHz, $CDCl_3$ 20°C): δ(ppm): 7.46-7.54(m), 7.27-7.30(m), 7.13-7.19(m), 6.93(s), 6.91(s), 3.91(t, ^2J(P-H) = 15.2 Hz, 2H), 3.17(m, 4H), 0.88(d, 24H). ^{31}P NMR: (250MHz, $CDCl_3$): δ-16 ppm Anal. Calcd for $C_{49}H_{56}N_2P_2$: $C_{49}H_{56}N_2P_2$:. C, 80.0, H, 7.6; N,3.8; Found: C,78.9; H, 7.45; N, 3.55; P, 7.85% MS(E1): m/z 733 (M^+).

Synthesis of MLX_2

Example 14

Ni(RNPPh$_2$ CH$_2$PPh$_2$NR)Br$_2$ R=Ph

To $NiBr_2$DME (1.77 mmol, 0.55 g) in THF, a slight excess of 1 $C_{37}H_{32}N_2P_2$ (1.77 mmol, 1.0 g) in THF was added at room temperature and immediate colour change was noticed and the solution stirred overnight. This resulted in a slightly coloured solution and green precipitate. The THF was filtered off and the solid dried under vacuum. The product was isolated as a green powder. (Yield: 88%, 1.22 g, 1.55 mmol). MS(FAB) m/z 905 (MLX).

Example 15

Ni{RNPPh$_2$CH$_2$PPh$_2$NR}Br$_2$ R=2,4,6 Me$_3$-C$_6$H$_2$

This was synthesized by the above procedure using $NiBr_2$DME (1.4 mmol, 0.44 g) and $C_{43}H_{44}N_2P_2$ (1.55mmol, l g). The product was obtained as a green powder. (Yield: 90%, 1.09g, 1.3 mmol). MS (FAB) m/z 789 (MLX).

Example 16

Ni{RNPPh$_2$CH$_2$PPh$_2$NR}Br$_2$ R=2,6 ^{i}Pr$_2$-C$_6$H$_3$

This was synthesized by the above procedure using $NiBr_2$ DME (0.71 mmol, 0.219 g) and $C_{49}H_{56}N_2P_2$ (0.71 mmol, 0.51 g). The product was obtained as a green powder. (Yield: 95 %, 0.67 mmol, 0.64g). MS(FAB) m/z 936 (MLX) IR: 1436cm^1(P=N).

Example 17

Co{RNPPh$_2$CH$_2$PPh$_2$NR}C1$_2$ R=Ph

This was synthesized by the above procedure using $CoCl_2$ (2.1 mmol, 0.27 g) and $C_{37}H_{32}N_2P_2$ (2.1 mmol,1.18 g). The product was obtained as a blue

powder. (Yield: 91 %, 1.9 mmol, 1.46 g). MS (FAB) m/z 660 (MLX).

Example 18

$Co\{RNPPh_2CH_2PPh_2NR\}Cl_2$. R=2,4,6 $Me_3C_6H_2$

This was synthesized by the above procedure using $CoCl_2$ (0.768 mmol, 0.1 g) and $C_{43}H_{44}N_2P_2$ (0.768 mmol, 0.50 g). The product was obtained as a blue powder. (Yield: 95 %, 0.729 (MLX).

Example 19

$Co\{RNPPh_2CH_2PPh_2NR\}Cl_2$ R=2,6$^iPr_2$-C_6H_3

This was synthesized by the above procedure using $CoCl_2$ (0.68 mmol, 0.088 g) and $C_{49}H_{56}N_2P_2$ (0.68 mmol, 0.5g). The product was obtained as a blue-green powder. (Yield: 93 %, 0.63mmol 0.55 g). MS(FAB) m/z 827 (MLX) IR: 1436cm^1(P=N).

Example 20

$Ni\{RNPPh_2CHPPh_2NR\}Br$. R=2,4,6 [$Me_3C_6H_2$]

To $C_{43}H_{44}N_2P_2$ (0.65 g, 0.92 mmol) in 50 ml THF, ^nBuLi (0.6 ml, 0.92 mmol) was added at -78°C. After stirring for half an hour and warming to room temperature, $NiBr_2DME$ (0.28g, 0.92 mmol) was added and the solution stirred overnight. The solvent was removed under vacuum from the resulting blue/green solution, CH_2Cl_2 was added and the resulting purple/blue solution was filtered and kept at -20° C. A purple crystalline solid was isolated (Yield: 50%, 0.39g, 0.5mmol).

Example 21

$Ni\{RNPPh_2CHPPh_2NR\}Br$, R=2,6$^iPr_2C_6H_3$

This was synthesized by the above procedure using $C_{49}H_{56}N_2P_2$(0.64 g, 0.87 mmol), ^nBuLi (0.55ml, 0.87 ml) and $NiBr_2DME$ (0.27g 0.87mmol). A purple crystalline solid was isolated (Yield: 52%, 0.40g, 0.46mmol).

Catalyst Evaluation

Catalyst evaluation was carried out in a stirred 1L autoclave operated in slurry mode using isobutane solvent. Agitation was carried out using a paddle stirrer and heat exchange carried out via the autoclave jacket.

Before catalyst evaluation the autoclave was cleaned, assembled and baked out by heating to 95°C and purging the vessel with dry O_2 free N_2 for 1 hour. The vessel was then cooled down under N_2 to about the polymerisation temperature.

Data logging was started and the catalyst injection system purged with N_2.

Catalyst solutions were then injected into the autoclave using N_2 overpressured. Polymerisation was allowed to continue, ethylene being taken up on demand. After the test period the ethylene gas was isolated, the reactor cooled, depressurised and the polymer unloaded.

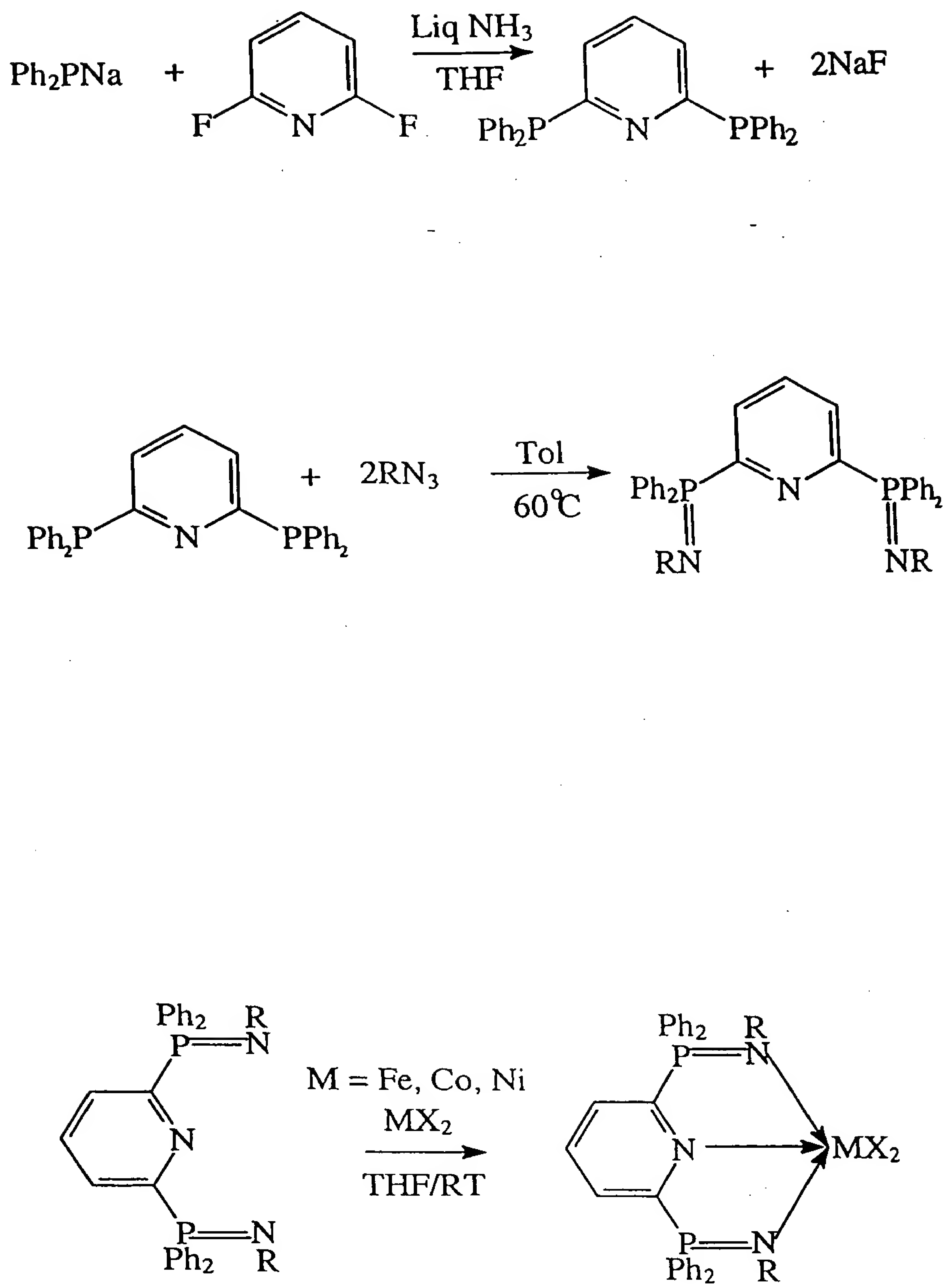
Results are given below in the Table.

The complex used for polymerisation were as follows:

EXAMPLE	COMPLEX
A	$Fe\{2,6.C_5H_3N(PPh_2NR)_2\}Br_2$ $R=2,6^iPr_2C_6H_3$
B	$Co\{2,6\text{-}C_5H_3N(PPh_2NR)_2\}Cl_2$ $R=2,4,6 - Me_3C_6H_2$
C - G	$Co\{RNPPh_2CH_2PPh_2NR\}Cl_2$ $R=2,6^iPr_2C_6H_3$

TABLE 1

Example	Catalyst used/mg	Run T /oC	Run P bar	Run time/h	Yield of PE/g	Activity g/gMetal/hr/b	Activity g/mmol/hr/bar	Mn/ g/mol	Mw/ g/mol	Mw/Mn	Mpk/ g/mol	MAO:cat. ratio
A	4.9	50	10	4.50	1.20	91	5	168000	392000	2.3	379000	1040
B	7.4	50	10	1.08	trace polymer	----	---	112000	231000	2.1	177000	570
C	5.8	30	10	1.00	1.80	463	27	76000	369000	4.9	278000	673
D	6.2	50	10	0.67	6.30	2273	132	48000	396000	8.2	68000	574
E	5.1	80	10	1.33	0.62	136	8	90000	153000	1.7	98000	765
F	8.6	30	10	1.0	1.0	210	12					905
G	6.5	80	10	1.0	1.0	229	13					1000



Ph2PNa
Liq NH3
THF
F
N
F
Ph2P
N
PPh2
2NaF
2RN3
Tol
60℃
Ph2P
N
PPh2
RN
NR
Ph2
R
P
N
M = Fe, Co, Ni
MX2
THF/RT
MX2

FIGURE 1

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